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Effect of cylindrical cavity height on laser-induced breakdown spectroscopy with spatial confinement

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Abstract

In this paper, we present a study on the spatial confinement effect of laser-induced plasma with a cylindrical cavity in laser-induced breakdown spectroscopy (LIBS). The emission intensity with the spatial confinement is dependent on the height of the confinement cavity. It is found that, by selecting the appropriate height of cylindrical cavity, the signal enhancement can be significantly increased. At the cylindrical cavity (diameter = 2 mm) with a height of 6 mm, the enhancement ratio has the maximum value (approximately 8.3), and the value of the relative standard deviation (RSD) (7.6%) is at a minimum, the repeatability of LIBS signal is best. The results indicate that the height of confinement cavity is very important for LIBS technique to reduce the limit of detection and improve the precision.

Keywords: LIBS, spatial confinement, cavity height, signal enhancement

(Some figures may appear in colour only in the online journal)

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a method of atomic emission spectroscopy (AES) that uses a laser-generated plasma as the hot vaporization, atomization, and excitation source [1]. LIBS is performed by focusing the laser on a small area at the surface of the specimen of interest, which is then ablated on a scale ranging from nanograms to picograms, and a plasma plume can be generated. In the past few decades, LIBS has been applied in a lot of fields, and can be used to analyze any matter, regardless of its physical state, whether it is solid, liquid, or gaseous [2–5]. LIBS was described as 'a future super star' in a 2004 review article by Dr James Winefordner, a world-renowned analytical spectroscopist [6]. This technique is only limited by the energy and pulse width of laser, the wavelength range of the spectrometer, and the sensitivity of the light detector.

In recent years, many researchers have attempted to improve the sensitivity of LIBS, such as plasma spatial confinement [7, 8], magnetic field [9, 10], fast spark discharge [11], use of ultra-short laser [12], external electric fields [13–15], flame-enhanced LIBS [16, 17], nanoparticle-enhanced LIBS [18], resonance-enhanced LIBS [19], double-pulse laser excitation [20–22], introduction of inert gas [23], and usage of the spectra normalization method [24, 25]. Among these methods, the additional instrument of the spatial confined LIBS is simple compared with other LIBS systems; the spatial confinement can effectively enhance the emission intensity of

LIBS. In the last decade or so, cavities with different shapes (typical examples: a pair of plates [26–28], cylindrical cavity [29–31], and hemispherical cavity [32–34]) are used to confine the laser-induced plasma, and the spectral emission, enhanced by the cavity, is observed and discussed [26, 35, 36].

The spatial confinement effect is devoted to improving the signal intensity in LIBS measurement. Yeates and Kennedy reported visible emission spectroscopy [28], visible intensified gated imaging and electrostatic probe analysis of laser plasma plumes generated within aluminum rectangular cavities of a fixed depth 6 mm and varying width (2.0, 1.5, and 1.0 mm), for comparison with the freely expanding plasma plumes generated from planar targets [37–40]. Fu *et al* investigated the synchronous behaviors of both a laser-induced plasma and shockwave on a flat surface and in a rectangular groove cavity [36]. Gao *et al* investigated the influence of the distance of the parallel plates on the laser-induced Cu plasma. The fast imaging and shadowgraph results showed that the shape of the plasma plume became narrower and longer with spatial confinement, and is also dependent on the wall distance [26]. Shen *et al* used a pair of plates to confine the plasma; the plumes were produced in between two parallel walls [27]. Guo *et al* investigated the enhancement of lines using hemispherical confinement of plasmas in LIBS. Laser-induced plasmas were produced and confined within the hemispherical cavity. The optical emission spectra of the plasmas and the temperature of the plasma plumes were investigated to study the evolution of the plasma [33, 41]. Shen *et al* studied the cylindrical confinement within a round pipe. LIBS was produced and confined inside the pipe. The depth of the pipe was 20 mm. The diameters of the pipes used for the experiments were 4.8, 10.8, 13.7, and 20.0 mm, respectively [30]. Hou *et al* demonstrated that the signal repeatability could be increased by using the cylindrical cavity with a 1.5 mm height and 3 mm diameter [29].

From the content described above, it is easy to know that the cavity shape will affect the intensity of confined plasma emission. Li *et al* fabricated the cylindrical cavities with different heights (1, 2, and 3 mm) and different diameters (3, 4, and 5 mm). Spatially and temporally resolved spectral emission profiles were measured to show the effects of cylindrical cavities of different dimensions on the plasma emission [31]. Su *et al* reported that two collinear pulse laser beams and a cylindrical cavity are combined together to generate and confine the laser-induced plasma and are used to evaluate the performance of the confined collinear dual-pulse LIBS [42]. The optimized cavity size for the best signal quality of the laser-induced plasma emission on a brass sample was obtained by varying cylindrical cavities [43].

To date, few detailed researches on the height of confined cavity have been carried out. In this work, the aim is to investigate the effect of the cylindrical cavity height on LIBS with the spatial confinement. Laser-induced silicon plasmas are produced and confined inside the cylindrical cavity with a fixed diameter and different heights. The optical emission spectra of the plasmas are studied.

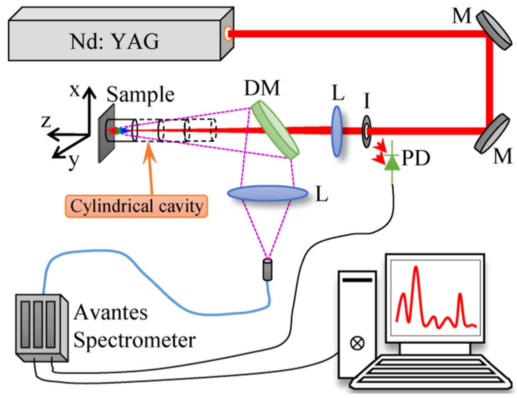

Figure 1. Experimental setup for nanosecond laser-induced Si plasma with cylindrical confinement. The components include mirror (M), iris (I), lens (L), DM (dichroic mirror), and photodiode (PD).

2. Experimental setup

The schematic drawing of the experimental setup used in this study for optical emission spectroscopy is shown in figure 1. The laser system is a Q-switched Nd:YAG laser (Continuum, Surelite III). The full-width at half maximum (FWHM) of the pulse is 10 ns, the maximum output energy is approximately 800 mJ, the wavelength is 1064 nm, and the repetition rate is 10 Hz. Laser-induced plasma is performed by focusing the laser pulses on the sample in air. The sample (p-type Si⟨100⟩, MTI KJ Group, 500 ± 10 μm thickness) is mounted on a computer-controlled X-Y-Z stage (Thorlabs, PT3/M-Z8), which guarantees that the sample location is renewed before each laser shot. The surface of the sample is placed at an angle of 90° with respect to the direction of the laser beam. The cylindrical confinement cavities are placed tightly on the surface of the sample, and the plasma plumes are generated in the center of the cylindrical cavity. The diameters of the cavities used for the experiments are 2 mm, and 4 mm. The heights of the cavities are 2 mm, 4 mm, 6 mm, 8 mm, 10 mm, and 12 mm, respectively. The emission spectra are reflected by a dichroic mirror between the sample and focusing lens, which is placed at an angle of 45° to the laser beam. The dichroic mirror is transparent to the laser light of 1064 nm but reflective to the visible light. The reflected spectra are focused on a fiber using a lens (BK7), which are orientated parallel to the laser beam. The fiber tip is positioned using a manual 3D translation stage. The spectra are guided to a spectrometer (Avantes, AvaSpec-ULS2048) through the fiber. The delay time is set to 0 μs. The exposure time is set to 1 ms (minimum time). A photodiode receives the scattered light of the iris to trigger the spectrometer, which guarantees time synchronization of the laser signal and the spectral signal. The final measured data is recorded by a computer. Each data point is typically an average of 50 shots. The entire experiment is carried out in air at atmospheric pressure.

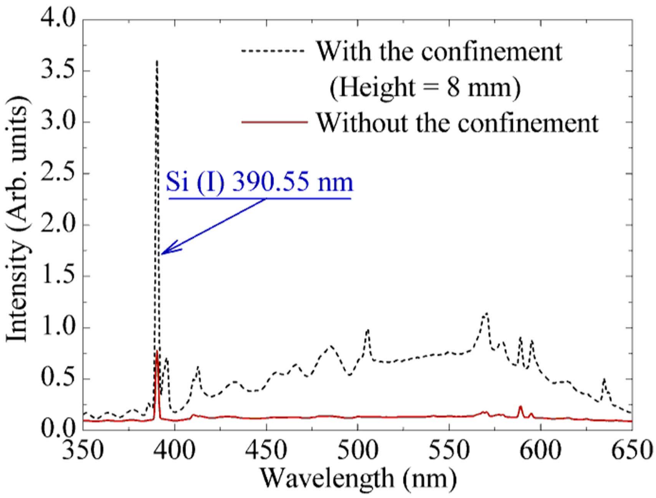

Figure 2. Comparison of spectral intensity in the range from 350 nm to 650 nm for laser-induced Si plasma with spatial confinement (diameter = 2 mm, height = 8 mm) and without spatial confinement. Laser fluence is 7.6 J cm^{-2}.

3. Results and discussion

The previously published papers show that many experimental conditions can change the emission intensity in LIBS, including the physical properties of the targets, the laser wavelength, pulse width, laser intensity, and so on [44–47]. During the expansion of laser-induced plasma plume in air, the plasma plume from an ablated target generates a shockwave [48], which in turn influences the overall LIBS process. If the shockwave hits the walls during the propagation of the shockwave, the shockwave will be reflected. The reflected shockwave can compress the plasma plume, so that the spatial confinement effect takes place [26]. Figure 2 compares the time-integrated spectral intensities of laser ablation of silicon with the cylindrical spatial confinement cavity (diameter = 2 mm, height = 8 mm) and without the spatial confinement over the range from 350 nm to 650 nm. Laser fluence is 7.6 J cm^{-2}. The strongest spectral line of Si plasma emission observed from this figure is Si (I) at 390.55 nm with the transition of $3s^23p^2\ (^1s_0) \leftarrow 3s^23p4s\ (^1P_1)$. As can be seen from figure 2, the emission intensity with the spatial confinement is higher than that without the spatial confinement. The spectral intensity for the Si (I) 390.55 nm is enhanced when the cylindrical cavity is presented. The enhancement factor is approximatively 5. The continuous spectrum in the range from 520 nm to 550 nm is also enhanced; the enhancement factor is also approximatively 5. The change of continuous spectrum is proportional to that of the characteristic spectral line.

As we know, the emission intensity for spectroscopy, corresponding to a transition from level k to i, is given by $I_\lambda = F_{\exp} N (A_{ki} g_k/(\lambda U(T_p)))(\exp(-E_k/(k_b T_p)))$ [49]. Here, A_{ki} is the transition probability, g_k and E_k are the degeneracy and energy of the upper level k, $U(T_p)$ is partition function, λ is the emission wavelength, k_b is Boltzmann constant, N is the total number density of a species in a given ionization stage, T_p is the plasma temperature, and $F_{\exp}$ is the experimental coefficient with respect to the efficiency of the optical detection system. According to this equation, most of the parameters are considered to be unchanged. Therefore, for a specific spectral line, the change of emission intensity is attributed to the change in the temperature and the total number density of the species in the plasma caused by changing the experimental conditions. In figure 2, the enhancement of spectral line is caused by the increase of the plasma temperature and density. The increase of the plasma temperature and density based on the spatial confinement effect is caused by the reflection of the shockwave from the wall of the confined cavity [36]. In general, LIBS is performed by focusing the laser on a small area at the sample surface in air, the plasma plume is formed, and a shockwave is generated by the abrupt deposition of energy into a small volume in the focal spot region. The shockwave usually expands at a higher speed, which is higher than the speed of a sound wave in air. In LIBS with the spatial confinement, different from the free propagated shockwave without the spatial confinement [37–40], when the shockwave arrives at the surface of the confinement cavity, the shockwave will be reflected by the inside surface of the confinement cavity. The shockwave continues to propagate back to the plasma plume, and subsequently interacts with the plasma plume. The reflected shockwave can compress the plasma to a smaller volume, enhancing the plasma temperature and density [26, 36]. Therefore, the emission intensity of plasma can be improved by shockwave heating due to the enhancement of plasma emission.

During the laser-produced plasma, the plume expands freely and rapidly along the opposite direction of the laser beam (plume expansion direction). The distance between plume front and sample surface may reach a few millimeters, and the effective length of the plume may reach 2–3 mm [13, 50, 51]. If the height of the cylindrical cavity is smaller than the position of the plume front, the cylindrical cavity will not be able to effectively confine the plasma plume. Therefore, the height of the cylindrical confinement cavity is very important to compress the plasma size and enhance plasma emission. Figure 3 shows the comparison of spectral intensity in the range from 350 nm to 650 nm for laser-induced Si plasma by using different cylindrical cavities with six heights (2, 4, 6, 8, 10, and 12 mm). Cavity diameter is 2 mm. Laser fluence is 7.6 J cm^{-2}. The height of the cavity not only affects the characteristic line, but also affects the continuous spectrum. The peak intensity of Si (I) 390.55 nm with the cylindrical cavity height (Diameter (Di) = 2, and 4 mm) and without the confinement is presented in figure 4. As can be seen from this figure, for the cavity with a diameter of 2 mm, the line intensity firstly increases and then decreases with the increase of the cavity height, it arrives at the maximum at a height of 6 mm. When the height of the cylindrical cavity increases, the effective length of plasma plume confined by the cavity increases. The cavity with a larger height is more efficient than that with smaller height to reflect the shockwave and compress the plasma plume, the enhancement of optical emission from laser-induced Si plasmas is stronger. Until the

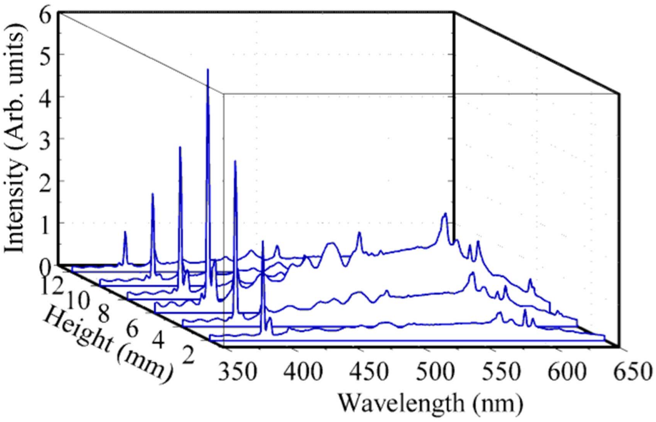

Figure 3. Comparison of spectral intensity in the range from 350 nm to 650 nm for laser-induced Si plasma by using different cylindrical cavities with six heights (2, 4, 6, 8, 10, and 12 mm). Cavity diameter is 2 mm. Laser fluence is 7.6 J cm^{-2}.

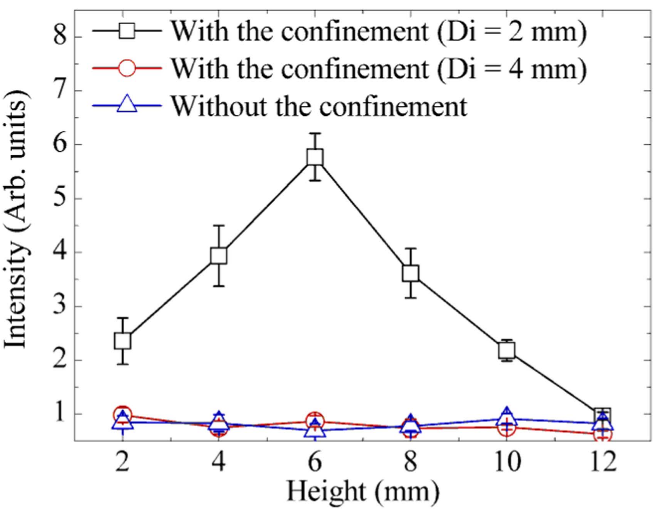

Figure 4. Evolution of spectral intensity of Si (I) 390.55 nm with the cylindrical cavity height (diameter = 2, and 4 mm) and without with the confinement. Laser fluence is 7.6 J cm^{-2}.

cavity can completely confine the plasma. Continuing to increase the cavity height will cause a part of plasma emission to be shaded (as shown in figure 1). Therefore, the plasma emission collected by the mirror and focusing lens decreases. However, when the cavities with the diameter of 4 mm are used to confine the plasma plume, the spectral intensity is almost equal to the spectral intensity without the spatial confinement. As the cavity diameter increases, the emission intensity temporal evolution profile will markedly change, the enhancement effect occurs later and becomes weaker [26, 27, 30]. At the early stage of plasma, the shockwave and plasma emission are very strong [52] so that the compression effect of the shock wave is the best. With the increase in distance, the delay time enhancement effect occurs later. Although the enhancement effect still can take place, in the whole integral delay time, the enhancement is relatively weak. Therefore, the contribution of spectral intensity is small, and the change of spectral intensity can almost be ignored.

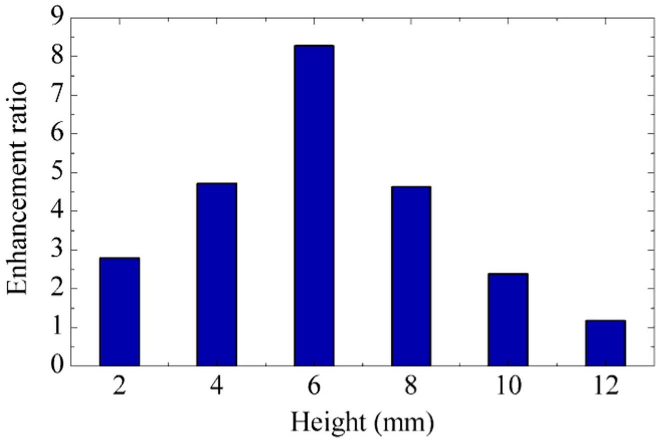

Figure 5. Enhancement ratio versus the cylindrical cavity height for Si (I) 390.55 nm.

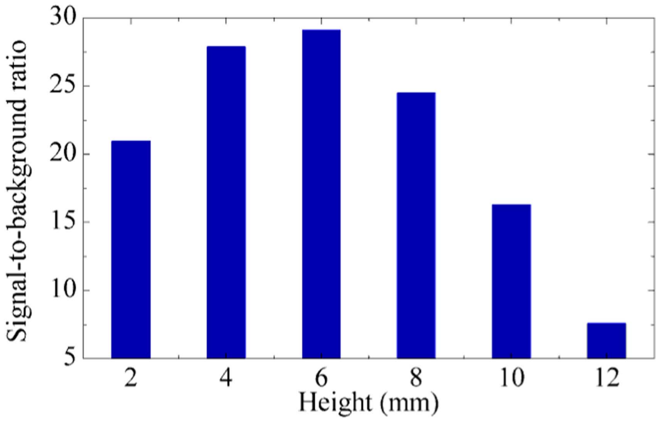

Figure 6. Signal-to-background ratio versus the cylindrical cavity height for Si (I) 390.55 nm.

Figure 5 compares the enhancement ratio of Si (I) 390.55 nm at the different heights with a diameter of 2 mm. The enhancement ratio of the emission intensity is calculated from the results in figure 4 by dividing the emission intensities with the cylindrical cavity of diameter 2 mm by the emission intensity without the spatial confinement. The change of enhancement ratio is similar to that of the emission intensity. The enhancement ratio with the cylindrical cavity of height 6 mm is higher than that with the other heights. The maximum value of the enhancement ratio is approximately 8.3. However, the enhancement ratio value is only about 1.2 when the height of the cylindrical cavity is 12 mm, and the enhancement ratio is smaller than that with the cylindrical cavity of 2 mm height. Therefore, we can optimize the emission intensity of LIBS with the spatial confinement by varying the height of the cavity. Figure 6 shows the signal-to-background ratio of Si (I) 390.55 nm at the different heights with the diameter of 2 mm. The change of signal-to-background ratio is similar to the change of enhancement ratio.

In the element analysis technique of LIBS, the stability of spectral intensity is important for the reliability and precision to measure elemental concentration. The relative standard deviation (RSD) is a special form of the standard deviation.

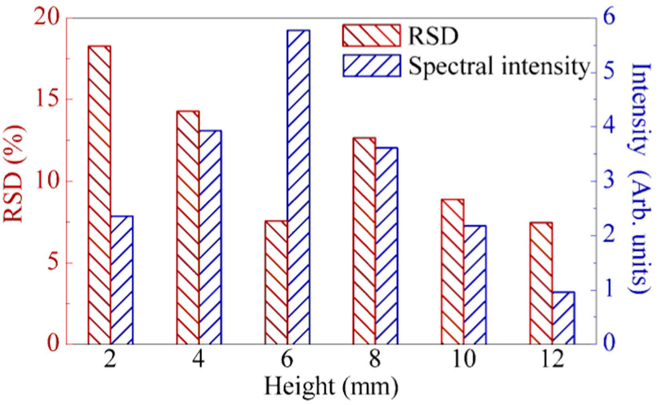

Figure 7. Relative standard deviation (RSD) and spectral intensity versus the cylindrical cavity height for Si (I) 390.55 nm.

The RSD is widely used in analytical chemistry to express the precision and repeatability of an assay. Researchers are often concerned about the problem of the precision and repeatability. Figure 7 shows the RSD and spectral intensity with the cylindrical cavity height of diameter 2 mm for Si (I) 390.55 nm. As can be seen from this figure, the height of cavity increases from 2 mm to 6 mm, the spectral intensity also increases while the RSD decreases from 18.3% to 7.6%. At the height of 6 mm, the value of RSD (7.6%) is minimum, the repeatability of LIBS signal is best. When the cavity height is changed from 6 mm to 8 mm, the RSD increases due to the reduction of spectral intensity. By continuing to increase the cavity height, the RSD and spectral intensity decrease. Therefore, the choice of confinement cavity height not only increases the intensity of spectral signal but also improves the signal repeatability. Then the limit of detection can be reduced, and the precision is improved.

4. Conclusions

In conclusion, we have demonstrated the enhancement of the optical emission generated by laser-induced Si plasma with the spatial confinement in the atmosphere. The cylindrical cavity is used to confine the plasma plume. The enhanced spectral intensity at the Si (I) 390.55 nm is dependent on the height of the confinement cavity. When the height of cylindrical cavity (diameter = 2 mm) increases from 2 mm to 12 mm, the plasma emission intensity including the characteristic line and continuous spectrum firstly increases and then decreases. At the cylindrical cavity with the height of 6 mm, the enhancement ratio is higher compared with the other heights. The maximum value of the enhancement ratio is approximately 8.3. At the height of 6 mm, the value of RSD (7.6%) is minimum, the repeatability of LIBS signal is best. This indicates that the height of confinement cavity is very important for the LIBS technique to reduce the limit of detection and improve the precision. These results may also be used to provide a better understanding to optimize the LIBS with the spatial confinement.

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